Antioxidant Properties of the Fatty Alcohol Esters of Gallic Acid

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PREVENTION of rancidity in fats and oils has received considerable attention during the last 15 to 20 years. Recently several reviews on the subject of antioxidants have been published (1,2,3,4). In general it is agreed that the polyphenolic compounds which have hydroxyl groups in ortho or para relation to each other are most effective. Powerful antioxidants of this type are nordihydroguaiaretic acid (NDGA) (5) and gallic acid.

One disadvantage of these antioxidants is their low solubility in fats and oils. This lack of solubility gives rise to technical difficulties in the process of incorporating the antioxidants into the fat.

The effect of fat solubility and the lipophilic character of an antioxidant on its carry-over into baked goods has been recognized for some time, but no systematic study has been reported. The fat solubility of a phenolic type of compound may be increased by introducing an alkyl group into the nucleus. A convenient method of improving the fat solubility of the hydroxybenzoic acids, for example, gallic acid, is esterification with fatty alcohols. A United States patent was issued to Sabalitschka and Böhm (6) in 1941 on the use of methyl, ethyl, propyl, and butyl gallates as antioxidants for fats and oils. These gallates have been classified among the best antioxidants. Furthermore, gallic acid and its esters in the small amounts required for use as fat antioxidants are generally considered non-toxic. Lea (1) pointed out that gallic acid is widely distributed as a constituent of the tannins present in many vegetable foods, particularly in tea. In recent pharmacological tests with mice (3) ethyl gallate was fed or injected in quantities greatly exceeding anything which would be taken in food stabilized with this substance. There were no apparent ill effects.

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In studying the effect of fat solubility on the carry-over into baked goods, it was considered desirable to use antioxidants of greater solubility than that of the lower gallates. For this purpose, therefore, the higher gallates—octyl, dodecyl, tetradecyl, hexadecyl, and octadecyl were prepared (7). These higher esters were readily soluble in fats and oils. The present paper is a continuation of this work and is a report on the evaluation of the antioxidant properties of these compounds.

Experimental

The lard used was a good-quality, steam-rendered lard consisting of 25% killing fats and 75% cutting fats. The hydrogenated vegetable shortening was a commercial grade purchased in the local retail market. The cottonseed oil was alkali refined and bleached.

Stability Tests: The modification of the active oxygen method (A.O.M.) previously described (8) was employed for evaluating the antioxidants in the fat substrates. The gallic acid and NDGA were incorporated by means of alcoholic solutions, and the solvent was removed as described in a previous paper (9).

Baking Tests: The effectiveness of the antioxidants in bakery goods was determined by piecrust tests. The recipe for the piecrust consisted of 100 g. pastry flour, 44 g. lard, 2.5 g. salt, and 33 cc. water. The pastry was mixed in a mechanical mixer and then rolled to one-eighth-inch thickness with a motor-driven sheeter. The dough was cut into round wafers one inch in diameter and baked on a sheet of aluminum at 200°C. for 17 minutes. The thermostatically controlled oven was of the reel type with four shelves which rotated vertically, so that the wafers were evenly exposed to the heat. In comparative baking tests, it is extremely important that the various batches of bakery products be browned to the same degree. The greater the degree of browning of a piecrust, the more rapidly rancidity will develop.

TABLE I.

Evaluation of Antioxidants at Different Concentrations.

Substrate	Antioxidant	Stability by the Active Oxygen Method					
		NDGA	Gallic Acid	Gallic Acid Esters			
				Propyl	Octyl	Dodecyl	Octadecyl
	%	*hours*	*hours*	*hours*	*hours*	*hours*	*hours*
Lard[1]	0.05	73	141	114	110	113	104
Lard	0.02	85	103	91	80	70	68
Lard	0.01	85	66	70	60	45	44
Lard	0.005	55	38	50	43	33	31
Lard	0.10	62	....	....	....	....	....
Lard	0.083[4]	....	....	....	106	....	....
Lard	0.10[4]	....	....	....	....	101	....
Lard	0.20	....	....	....	....	97	....
Lard	0.124[4]	....	....	....	....	....	108
Lard	0.05	199	....	294	....	229	....
HVO[2]	0.01	112	....	138	....	113	....
HVO	0.01	8	13	10	11	10	9
CSO[3]							

[1] Lard-control, 7 hours.
[2] Hydrogenated vegetable oil—control 78 hours.
[3] Cottonseed oil—control 8 hours.
[4] Concentration of the gallate is equal to the molecular equivalent of 0.05% gallic acid.

The wafers were placed in 6-oz. wide-mouth bottles, covered with small watch glasses, and stored at 38° C. and at 63° C. Rancidity was determined organoleptically.

Results and Discussion

The stability values on lard in Table I show a somewhat higher protective action for gallic acid than for its esters. The difference, however, is not so great as might be expected since the functional portion (gallic acid radical) of octadecyl gallate, for example, is only about 40% of its molecular weight. Thus, when gallic acid and the esters were added in equal molecular concentrations (gallic acid equal to 0.005% concentration, Table II) the esters gave greater protection than gallic acid. On the other hand, gallic acid at the high concentration of 0.05% gave somewhat higher protective action than did the esters in molecular equivalent amounts, Table I. This concentration, however, is above the optimum level for the esters. The differences between the individual esters may not be significant. None of the antioxidants gave much protection for cottonseed oil, whereas they markedly enhanced the stability of hydrogenated vegetable oil.

TABLE II.

Stability Values for Lard Containing 0.005% NDGA, 0.005% Gallic Acid, and Esters of Gallic Acid in Corresponding Molecular Equivalent Amounts.

Antioxidant	A.O.M. Stability
	hours
NDGA	43
Gallic acid	33
Propyl gallate	44
Hexyl gallate	55
Octyl gallate	52
Dodecyl gallate	42
Tetradecyl gallate	45
Hexadecyl gallate	54
Octadecyl gallate	55
None	8

The usual synergistic effects of certain acidic compounds were also noted. As shown by the stability values in Table III, isoascorbyl palmitate (6-palmityl-d-isoascorbic acid) was the most effective. In general, the synergists were more effective when used with NDGA than with the gallates.

The results of baking tests in which piecrust wafers were stored at two temperatures are shown in Table IV. The effectiveness or carry-over of the antioxidant properties of the higher gallate esters in piecrust was much superior to that of propyl gallate or gallic acid. This was true at both storage temperatures but was shown more strikingly in the tests at 63° C. When the antioxidants were added in 0.05% concentrations, rancidity developed in 1 and 3 days, respectively, in wafers containing gallic acid and propyl gallate, while 8, 9, and 10 days, respectively, were required for rancidity to develop in the wafers containing octyl, dodecyl, and octadecyl gallates.

TABLE III.

Evaluation of the Synergistic Effect of Phosphoric Acid, Isoascorbyl[1] Palmitate, and Citric Acid on Antioxidants in Lard.

Antioxidant	A.O.M. Stability			
	Without Synergist	With 0.01% H_3PO_4	With 0.02% Isoascorbyl[1] Palmitate	With 0.02% Citric Acid
	hours	*hours*	*hours*	*hours*
0.02% NDGA	79	105	147	109
0.02% Gallic Acid	93	....	133	....
0.02% Propyl Gallate	93	89	119	82
0.02% Octyl Gallate	71	....	103	....
0.02% Dodecyl Gallate	58	71	94	75
0.02% Hexadecyl Gallate	63	71	89	61
None	5.5	....	....	....

[1] 6-palmityl-d-isoascorbic acid.

Most antioxidants in oils have an optimum concentration, above which there is no appreciable increase in the protective value as measured by the active oxygen method. In Table I there was no increase in protective value when the concentration of the antioxidant was raised above 0.05%. In baking tests, however, the optimum concentration of antioxidants was considerably higher. In Tables IV and V, the results of baking tests indicate that the dodecyl and octadecyl gallates are much more effective at 0.1% concentrations than they are at 0.05%.

TABLE V.

Days Required for Development of Rancidity in Piecrust Wafers Made With Lard Containing 0.05% Gallic Acid and the Esters of Gallic Acid in Corresponding Molecular Equivalent Amounts.

Antioxidant	Days Required for Development of Rancidity	
	At 38° C.	At 63° C.
0.05% Gallic Acid	26	1
0.1% Dodecyl Gallate	>185	53
.124% Octadecyl Gallate	>185	79
0.1% NDGA	48	5
Control	18	2

In a few preliminary tests on baked crackers, the degree of carryover of the gallates was considerably less than that reported for piecrust wafers.

The substantially better carry-over of the antioxidant action of the higher gallates than that of gallic acid or propyl gallate suggests that fat solubility of the antioxidant is an important factor. More work with different series of compounds, however, is required before any general conclusions can be drawn.

Summary and Conclusions

The antioxidant properties of octyl, dodecyl, tetradecyl, hexadecyl, and octadecyl gallates in lard substrate were determined by the active oxygen method. The order of their effectiveness was about the same as that of the more active antioxidants, nordihy-

TABLE IV.

Days Required for Development of Rancidity in Piecrust Wafers Made With Lard Containing Different Amounts of Antioxidants.

Temperature of Storage	Antioxidant	Days Required for Development of Rancidity					
		NDGA	Gallic Acid	Gallic Acid Esters			
				Propyl	Octyl	Dodecyl	Octadecyl
	%						
38° C. Control, 18 days	0.05	49	26	35	60	46	60
	0.02	27	26	35	46	60	42
63° C. Control, 2 days	0.05	6	1	3	8	9	10
	0.02	2	1	2	5	6	4

droguariaretic acid and gallic acid, that have been reported. The carry-over of the antioxidant properties into baked goods was determined by storage tests on piecrust at 38° and 63°C. The results show that the higher gallates have good protective action in baked piecrust and are much superior to gallic acid and propyl gallate.

These higher esters of gallic acid are readily soluble in fats. This factor is of great importance in commercial stabilization of fats.

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